Short communication

Characterization of ceramic-metal composite hydrogen separation membranes consisting of barium oxide, cerium oxide, yttrium oxide and palladium

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Abstract

Cermet (ceramic-metal composite) hydrogen separation membranes consisting of barium oxide, cerium oxide, yttrium oxide and palladium were characterized by utilizing X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS). Characterization was performed at room temperature and 650 °C, and after exposure to hydrogen. Changes in both elemental composition and oxidation states were observed at elevated temperatures and as a function of time. Permeation of hydrogen through the membranes also changed with time and temperature.

1. Introduction

Researchers at Argonne National Laboratory (ANL) [1,2] are developing dense, mixed-conducting ceramic membranes to separate hydrogen from various gas streams at 550–850 °C (823–1123 K). These cermet membranes are composed of barium oxide, cerium oxide, and yttrium oxide (BCY). Metallic palladium was added to the oxide ceramics to promote nongalvanic hydrogen permeation. The membrane surface plays a critical role in determining the initial reaction, and it is important to understand the surface properties of these membranes.

The objective of this research is to characterize the surface properties of BCY-Pd membranes at both room and elevated temperatures. High temperature X-ray photoelectron spectroscopy (XPS) and high temperature scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) were utilized in this study.

2. Experimental

The experimental procedure for preparing BCY membranes with metals and the procedure for permeation

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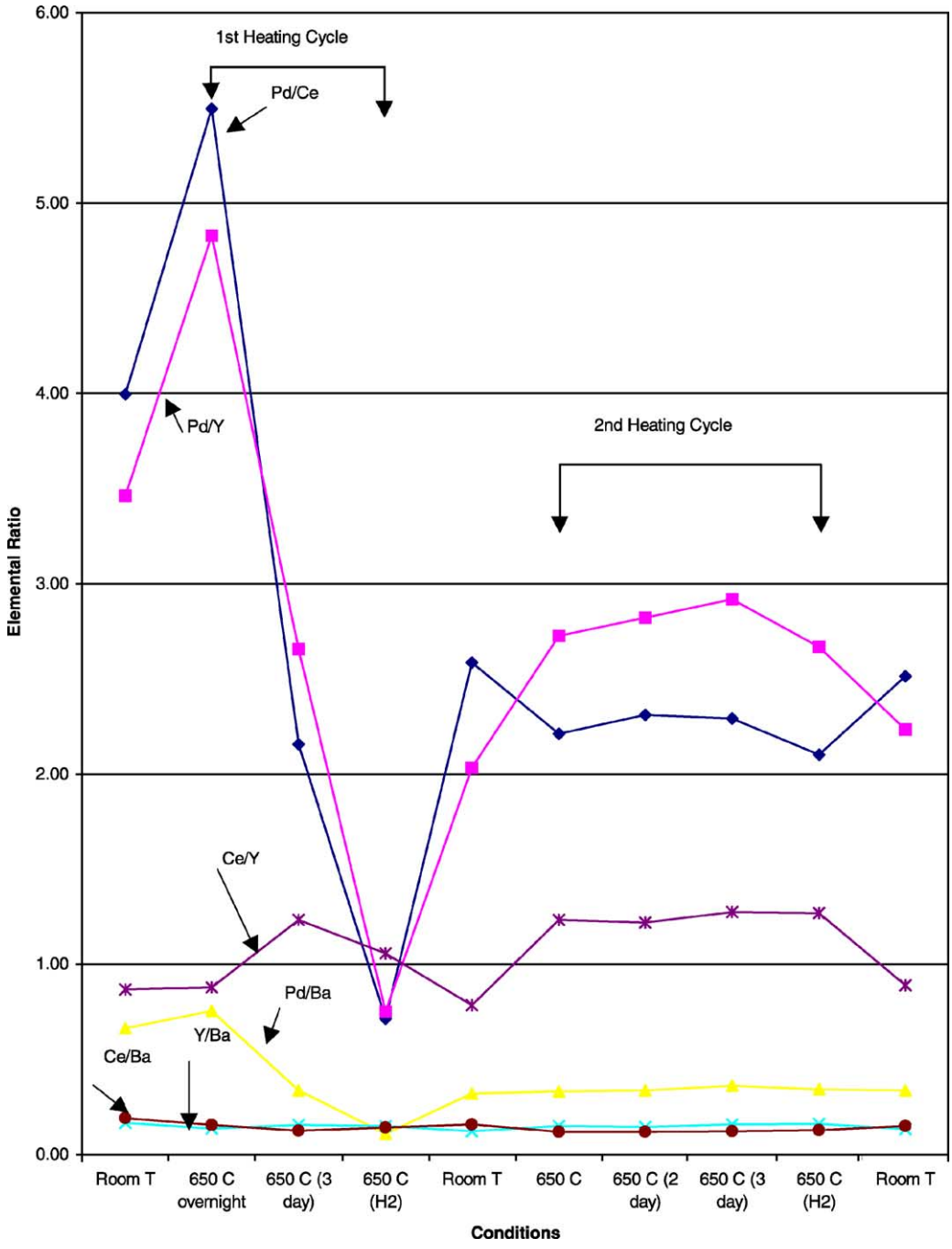

Fig. 1. Surface elemental ratios of thin membrane.

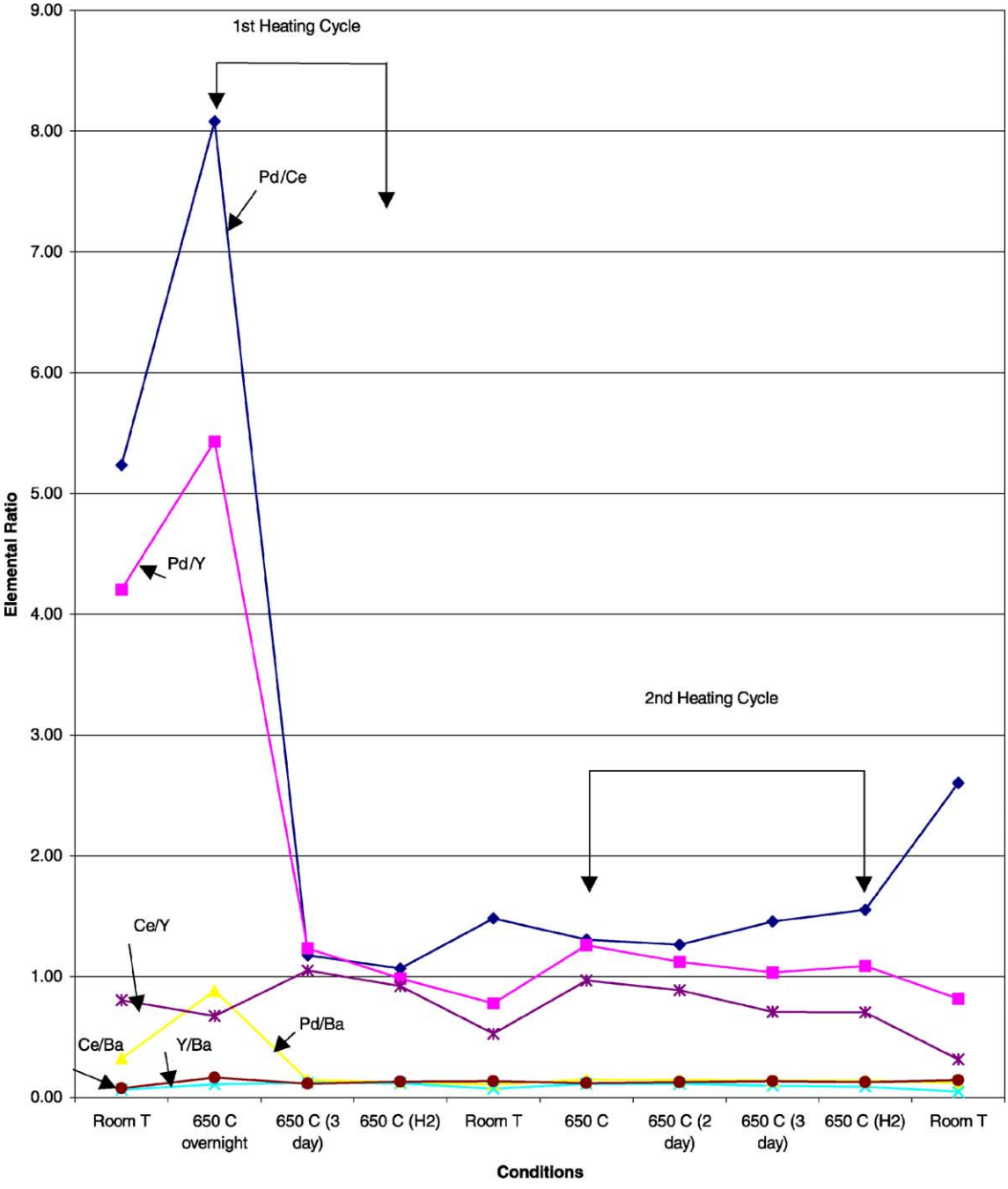

Fig. 2. Surface elemental ratios of thick membrane.

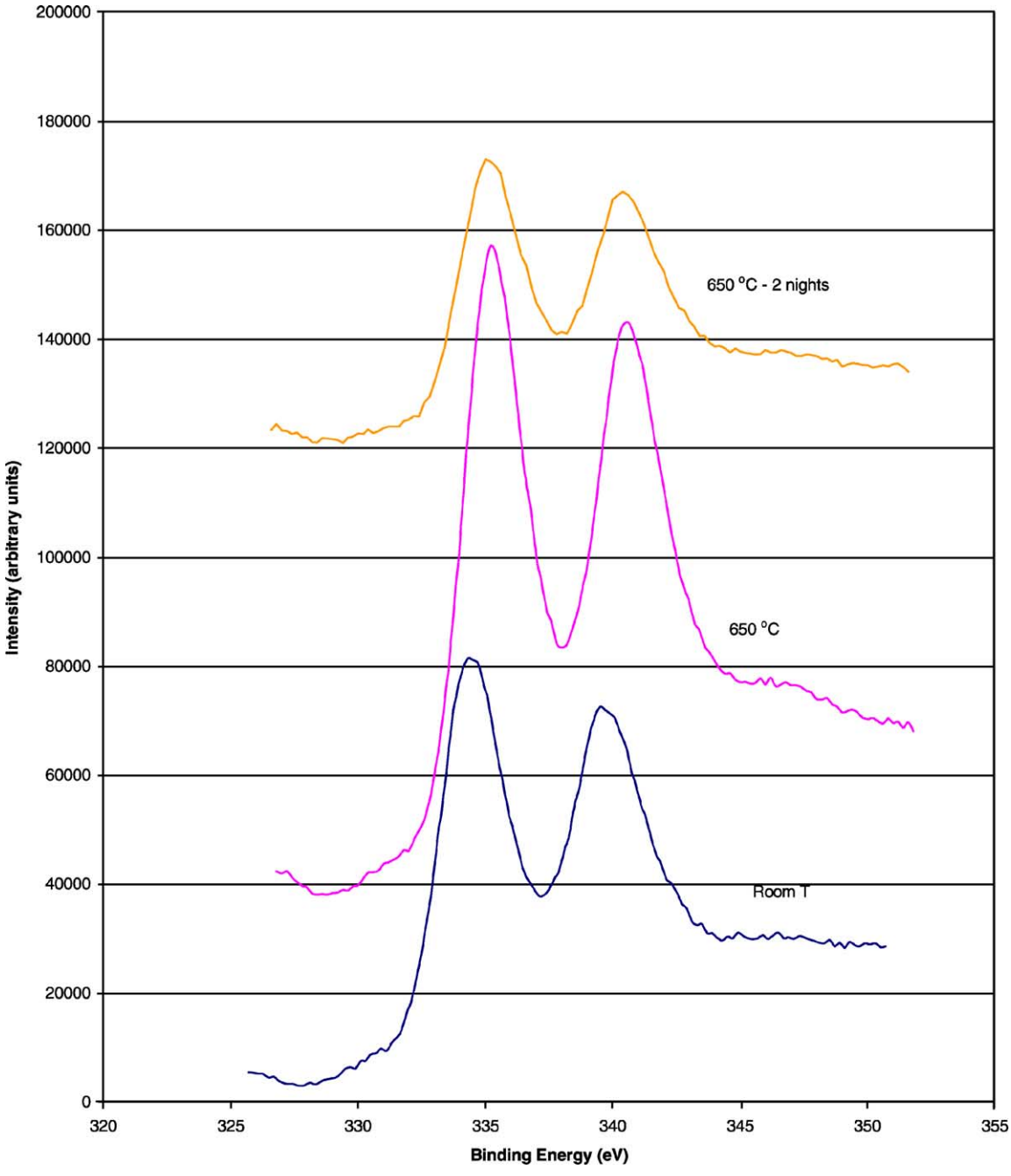

Fig. 3. Pd 3d peaks of thin membrane.

tests have been reported previously [1]. Experimental procedures for XPS and X-ray microanalysis with SEM/EDS are described in [2]. XPS and X-ray microanalysis were performed at an ambient temperature at 650 °C (923 K) for 1 and 3 days, after exposure to hydrogen at 6×10^{-5} Torr (7.9×10^{-3} Pa) for 1 h at 650 °C, and after cooling back to room temperature. This experimental sequence was repeated once more.

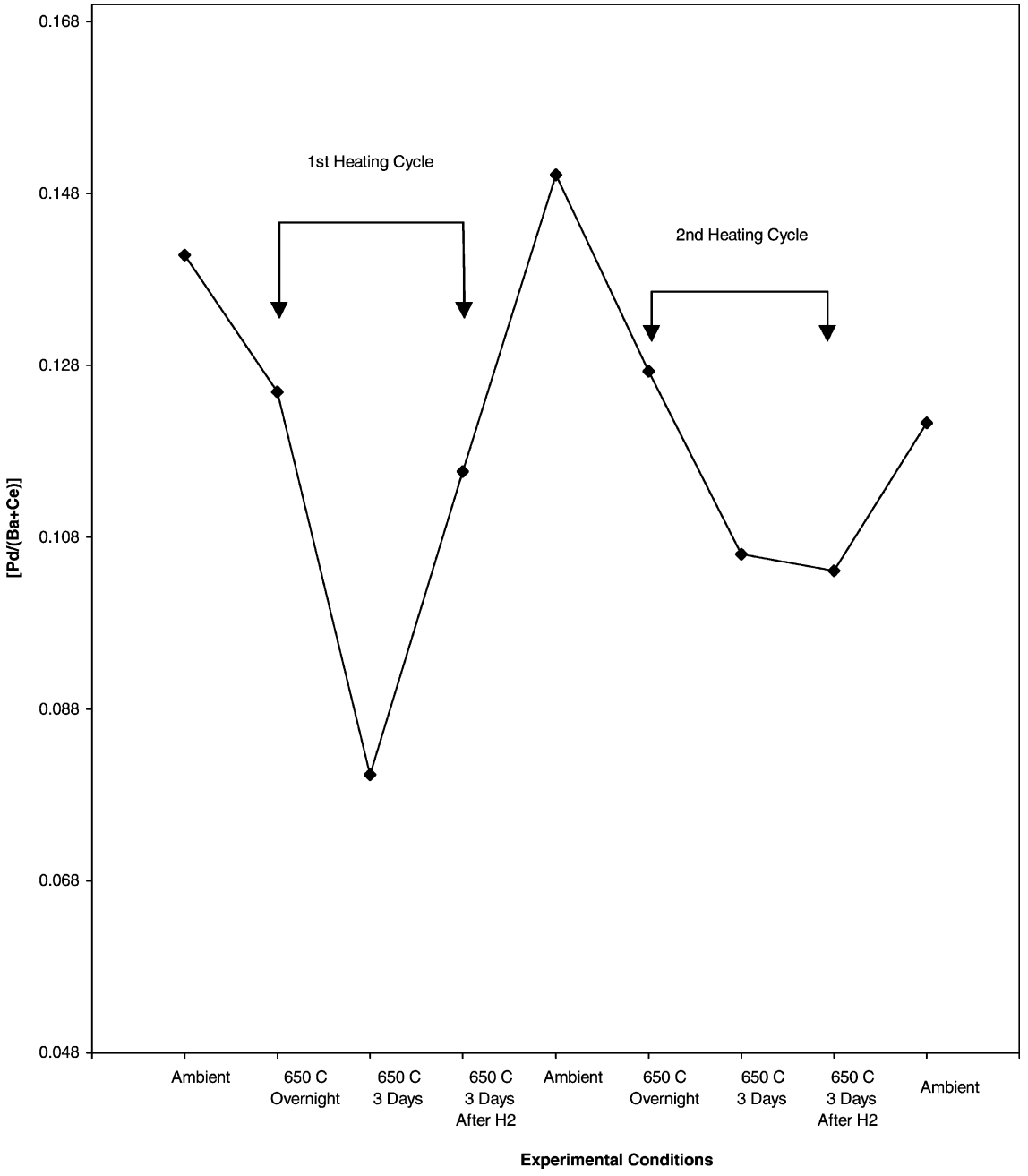

Fig. 4. SEM/EDS atomic ratios of thin membrane.

3. Results and discussion

Permeation of hydrogen was tested with two BCY-Pd membranes that have thickness values of 0.23 and 1.67 mm. Hydrogen permeation values measured by flowing 100% hydrogen on the feed side, and nitrogen with 100 ppm (0.01%) hydrogen on the sweep side of the two membranes at ambient pressure are listed in

Table 1
Permeation values of hydrogen in the membranes

Temperature (°C)	Permeability of thin (0.23 mm) membrane ($cm^3/(min\ cm^2)$)	Permeability of thick (1.67 mm) membrane ($cm^3/(min\ cm^2)$)
600	0.597	0.308
700	0.733	0.369
800	0.996	0.431
900	1.21	0.504

Table 1. In both membranes, permeability increased with increasing temperature. The hydrogen flux values were also measured as a function of time with a 0.44 mm thick membrane at 800 °C. The flux values increased from an initial value of 1.107–2.7776 $cm^3/(min\ cm^2)$ at 70 h, and a stable flux value was observed after 70 h. A similar observation was also made at 900 °C. It is interesting to note that the flux increased with increasing time and stabilized after 70 h. This indicates that the membrane underwent changes during the initial heating, but appeared to achieve stability after 70 h.

Elemental ratios obtained by XPS spectra of the thin membrane are shown in Fig. 1. The surface elemental composition changed as a function of both time and temperature. Elemental ratios changed drastically during the initial heating cycle. For instance, both Pd/Ce and Pd/Y initially increased with increasing temperature, but both ratios decreased when the temperature was kept at 650 °C for 3 days. During the next heating cycle, elemental composition changes were minimal, but the Pd/Ce ratio appeared to be lower and the Pd/Y ratio appeared to be higher at 650 °C than at room temperature. This indicates that elemental rearrangement takes place in the membrane during the initial heating cycle. A similar observation was made with the thick membrane (as shown in Fig. 2). The signal intensity of the Pd peak in both thin and thick membranes also increased during the initial heating from room temperature to 650 °C and decreased after 3 days at 650 °C (as shown in Fig. 3). Migration of nickel and copper to the surface at high temperature has been previously observed with desulfurization sorbents [3,4]. Similarly, migration of nickel has been observed with nickel containing membranes [2]. It has been postulated that the element with the most ability to get reduced to metal and the one with the most ability to get evaporated migrates to the surface [3]. XPS data indicated that palladium is in the metallic state (BE = 335.5 eV) and it is more likely that palladium would migrate to the surface at elevated temperature. However, it is not clear why the Pd/Y and Pd/Ce ratios at the surface decreased after 3 days of heating at 650 °C. Loss of Pd from the surface is very unlikely since the melting point of Pd is 1555 °C and the boiling point is 2963 °C. The cerium spectra at room temperature of both thick and thin membranes showed the absence of satellite structure at 916 eV. This indicated that cerium was mainly in the +3 oxidation state. When the sample was heated to 650 °C, there was some formation of Ce^{4+} (as indicated by the changes in the satellite structure).

The calculated value of the maximum depth of the X-ray interaction volume for X-ray microanalysis is approximately 0.7 μm. The plot of the Pd/(Ba + Ce) ratio of the thin membrane at various experimental conditions is shown in Fig. 4. It was not possible to fully differentiate the Ba and Ce peaks, because the peaks overlapped. There is a significant change in the Pd/(Ba + Ce) ratio during the initial cycle of heating at 650 °C for 3 days, but the change in the ratio was less significant in the second cycle similar to the observations with XPS data. A similar observation was made with the thick membrane.

The permeability of hydrogen through the membranes, at both 800 and 900 °C, increased with time for about 70 h before reaching a steady state. Elemental composition also changed, both at the surface (XPS data) and near surface (SEM/EDS), during the initial heating cycle for 3 days (∼70 h). The BCY-Pd membrane exhibits protonic conductivity that is significantly higher than its electronic conductivity. The incorporation of palladium enhances the electronic conductivity of the membrane. The migration of palladium to the surface at high temperatures will decrease the interfacial polarization resistance and this, in turn, will contribute to the increase in hydrogen permeation (N) of the membrane. However, depletion of the palladium in the bulk of the membrane will decrease the ambipolar conductivity, which will contribute to a decrease in the permeation rate. The initial increase in flux with time in these

membranes may be related to the rearrangement of palladium in the membrane observed during the initial heating cycle.

4. Conclusions

Elemental rearrangement was observed during the initial heating cycle at both the surface and near surface of the BCY-Pd. This was very significant with respect to palladium concentration. Changes in the hydrogen flux through these membranes was also observed initially during the hydrogen permeation tests, but stabilized after about 70 h. The changes in the flux may be related to the changes in elemental composition of the membranes.

Acknowledgements

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